Environmental Management and Sustainable Development
ISSN 2164-7682
2022, Vol. 11, No. 4

Determination of Heavy Metals in Black Sea Whiting Fish (*Merlangius merlangus,* Linnaeus, 1758) Species

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Received: June 10, 2022 Accepted: August 1, 2022 Published: August 11, 2022

doi:10.5296/emsd.v11i4.20162 URL: https://doi.org/10.5296/emsd.v11i4.20162

Abstract

The Black Sea is surrounded by numerous industrial and agricultural areas. Therefore, many land-based pollutants are released into the Black Sea. Discharge of industrial and agricultural untreated wastewater to the Black Sea from a single source or scattered sources has been reported.

The current study aimed to determine the concentration values of some heavy metals in the tissues of whiting fish (*Merlangius merlangus,* Linnaeus, 1758), one of the economical demersal species of the Black Sea. Accordingly, the accumulation concentrations of heavy metals including manganese (Mn), cobalt (Co), copper (Cu), zinc (Zn), and iron (Fe) were investigated in muscle tissue, gill, gonad, liver, and other visceral organs (except liver) in whiting fish samples.

Heavy metal concentrations determined in the muscle tissue, which are particularly important for human consumption and health were sorted as Fe>Zn>Cu>Co>Mn and the concentration values of metals were 82.84±7.11; 50.45±12.24; <0.818; <0.479; <0.413 $\mu g.kg^{-1}$, respectively. Zn had the highest concentration in gonad tissues whereas the highest concentration determined in the liver, visceral organs, and gills was Fe. As a result of the comparison of heavy metal results obtained in the muscle tissues with the relevant standards (FAO, 2010 and FAO/WHO, 2004), it was found that they were below the risky limit values for human

consumption.

Keywords: The Black Sea, Marine pollution, Heavy metals, Marine ecosystem

1. Introduction

The Black Sea is exposed to numerous pollutants such as metals, especially the coastal zone is affected by point and non-point waste and discharge of approximately 170 million people, (Gedik & Öztürk, 2019). In addition, the Black Sea region has very rich potential in terms of Cu, Zn, and Pb mineral reserves. Therefore, the wastes of the mentioned mines are transported to the marine environment by surface waters, as well as rivers and streams of various sizes (Cevik et al., 2008; Baltas et al., 2017; Mutlu, 2021).

The Black Sea has already been substantially negatively affected by unmanaged fisheries, unrestricted intense shipping activities, mineral exploitation, and the toxic waste disposals (Mee, 1992). Massive loads of domestic wastewater and industrial effluents have been transported by rivers and discharged into the Black Sea. As a consequence, organic, and inorganic pollutants have been accumulating in the Black Sea (Eremeev, 1995). These contaminants that enter the aquatic ecosystem may not directly negatively affect the organisms, however they may accumulate in aquatic organisms through the food chain process and eventually threaten human health through consumption (Bat et al., 2013a).

Non-essential metals including cadmium (Cd) and lead (Pb) is of particular significance due to their substantial different toxic effects on aquatic biota (Phillips & Rainbow, 1994). Essential metals can also potentially be hazardous to marine organisms. It has been stated that essential metals are hazardous environmental pollutants and are able to accumulate along the aquatic food chain with severe risk for aquatic organisms (Bryan, 1976) and human health (Underwood 1977; Bat et al., 2013b).

Approximately 93% of the whiting (*Merlangius merlangus*, Linnaeus, 1758) fish population in Turkey is found in the Black Sea. Whiting fish consumption has increased from 8,122 tons in 2011 to 8,700 tons in 2020 (Figure 1). In 2020, approximately 99.3% of the whiting fish caught were marketed for consumption (TurkStat, 2022).

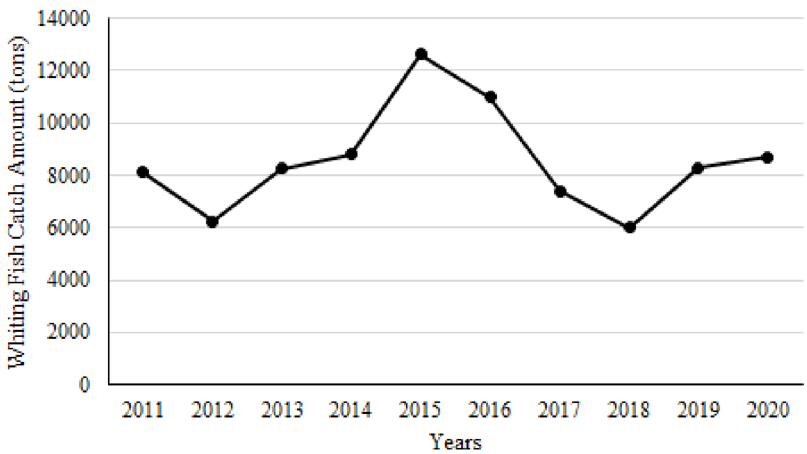

Figure 1. Whiting fish caught in the Black Sea Turkish waters in 2011-2020 (in tons)

The whiting fish was selected for the study since it is a species found in all seasons in the Black Sea. Also, it is a benthopelagic fish. Therefore, it has been thought that it may be more affected by metal deposits and the findings would even be more important. Also, whiting fish is a local species of the Black Sea. In the present study, heavy metals, cobalt (Co), manganese (Mn), zinc (Zn), iron (Fe), and copper (Cu) accumulation concentrations were investigated and examined in muscle tissues, liver, other visceral organs, gonad and gills of whiting fish samples obtained the Sinop Coasts of the Black Sea.

1.1 A Brief Assessment of the Black Sea pollution

The Black Sea has been getting more polluted day by day due to the land-based pollutants around the Black Sea. The Black Sea is exposed to heavy metal pollution, especially from pollutants from industrial and agricultural sources (Gökkurt Baki, 2011).

The pollution load of the Black Sea has increased due to the waste brought by the rivers from various countries, including Turkey. The Black Sea is rich in terms of marine plankton and fish that feed on this biomass. The Black Sea is Turkey's most important fishing area. However, the volume of fish caught has decreased in recent years. This was associated with overfishing on one hand and the fact that the marine ecosystem has been changing due to ballast water discharges from ships on the other (Turkish Environment Foundation, 2003). Also, there is an excessive pollutant load in the Black Sea region, especially in regions under the impact of rivers with large flow rates such as the Danube, Dnieper, and Dniester (Gomoiu, 1992).

Bat et al. has stated, “The Black Sea receives large volumes of unregulated and uncontrolled fresh water with drawl for irrigation purposes, hydro and thermal power generation and the use of coastal areas for permanent human settlements; shipping; and untreated domestic, industrial, and agricultural wastes drain into the sea via the rivers or directly”. However, research on the heavy metal pollution in marine biota of the Black Sea is very limited. Moreover, corresponding data on the pollution state of the Black Sea off Turkey are rare (Bat et al., 2009).

The present study examined the concentrations of heavy metal types including manganese (Mn), cobalt (Co), copper (Cu), zinc (Zn), and iron (Fe) in the muscle, gill, gonad, liver, and other visceral organs (except for the liver) of fish samples. The study aimed to update the results of the studies carried out so far and to determine the heavy metal concentrations in various tissues and organs of whiting fish, an important local species of the Black Sea ecosystem. Thus, it was thought that evaluations could be made in terms of environment and public health, and it would be possible to obtain data that guides the subsequent planning.

2. Material Method

2.1 Sample Preparation, Digestion, and Metal Analysis

The study was carried out on whiting fish caught from the Sinop (the Black Sea) coasts by the commercial fisheries (Figure 2). Fish samples were obtained from September to December 2011.

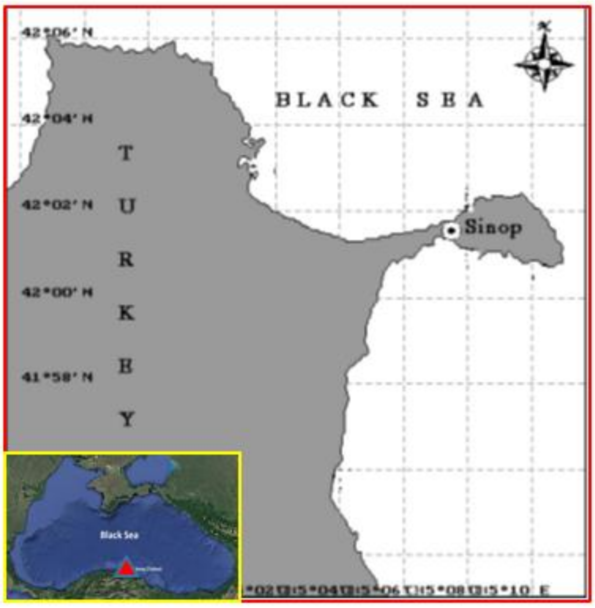

Figure 2. The image of the sampling area on the Black Sea coast of Turkey (N: 42 °0' 23.63" E: 35 °12' 10.19") (Google Maps, 2021)

The whiting fish samples (n=145) were provided from fish markets from September to December 2011. The average length and weight for the whiting fish are given in Table 1, Figure 3. The samples were then washed with deionized water.

Table 1. Biometric data of the whiting fish samples from the Black Sea Coast

	Average (±SD)	Min.	Max.
Length (cm)	24,46 ±0,60	10,2	48,3
Weight (g)	14,73 ±0,12	11,4	19,5

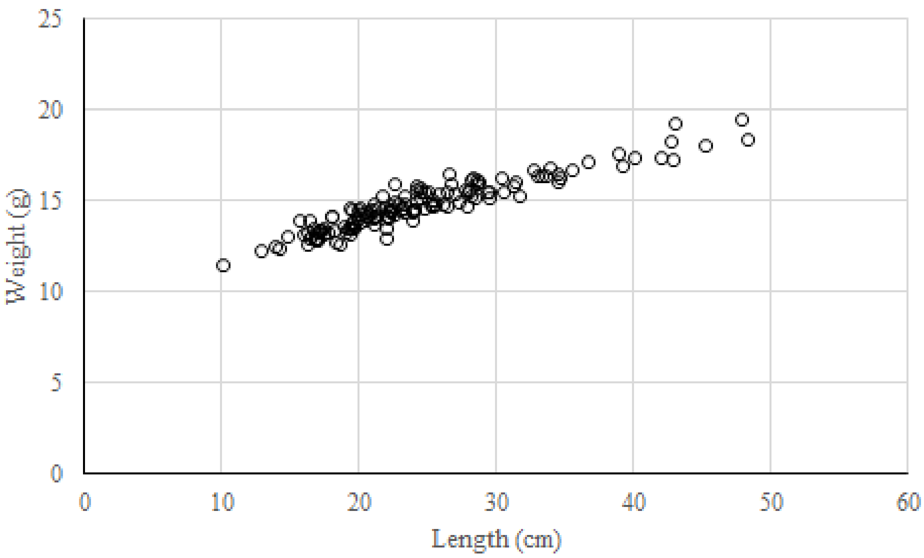

Figure 3. Length-Weight distributions of the fish samples

2.2 Sampling Collection, Preparation, and Analysis

Following the collection of the biometric data, the muscle, gill, gonad, liver, and visceral organ samples of the fish were removed (Figure 4).

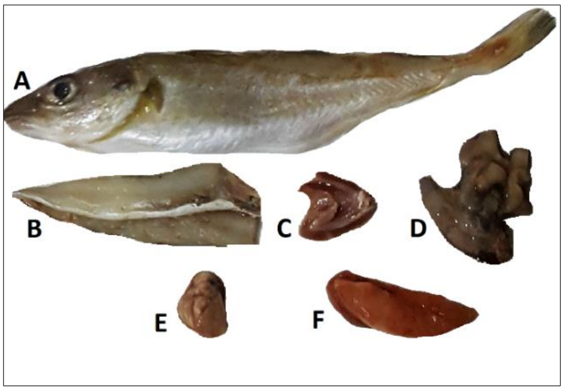

Figure 4. The preparation of the tissues and organs of the whiting samples A- Whiting fish, B-Muscle, C-Gill, D-Visceral organ, E-Liver, F-Gonad (original photo)

All the removed organs in the study were homogenously blended. The samples were packaged in three replications in plastic bags and stored under appropriate conditions (deep freezer at -20^{o}C) until the time of analysis.

Approximately 10 g samples were taken from the plastic bags, sterilized, placed in jars, and treated with concentrated nitric acid for the release of heavy metals. Before the analysis, the samples were filtered through a 0.45-µm-millipore membrane. Then, the samples were left to cool., and 1 ml HNO_3 was added to the residue. The mixture was taken into 25-ml-metered balloons and diluted to 15 ml with double-distilled water. The analyses were carried out in triplicate, and in each replicate, three repetitions were conducted to assess all potential cases. All heavy metal measurements were made using an Atomic Absorption Spectrophotometer (AAS).

2.3 Statistical Analysis

The differences between the obtained data were determined by the one-way ANOVA and the multiple Duncan multiple tests. The level of relationship between the tissues and metals was determined by the correlation analysis. The Tukey test was adopted for multiple comparison normal distributions and the Kruskal-Wallis test was utilized for non-normal distribution. All statistical analyses were carried out using the SPSS 21 statistical software program. The significance level of the data was set as 0.01 and 0.05, the P values lower than 0.01 and 0.05 were considered statistically significant.

3. Results

3.1 Heavy Metal Concentrations in Whiting Fish

The healthiest way to determine this case is to do research and compare the obtained findings with the standard values. The average values of heavy metal results (µg.kg^{-1}) determined in different tissues of whiting fish in the study are given in Table 2 and Figure 5.

Table 2. Heavy metal concentrations determined in whiting fish (*Merlangius merlangus*, Linnaeus, 1758) samples (µg.kg^{-1})

	Mn	Fe	Co	Cu	Zn
Liver	16,11 ±0,47^{b,y}	550,48 ±41,89^{d,z}	<0,479^{a,y}	<0,818^{a,z}	275,88 ±80,16^{c,y}
Muscle	<0,413^{a,w}	82,84 ±7,11^{c,x}	<0,479^{a,y}	<0,818^{a,z}	50,45 ±12,24^{b,w}
Gonad	3,47 ±0,24^{b,x}	151,19 ±8,96^{c,y}	<0,479^{a,y}	<0,818^{a,z}	418,75 ±54,11^{d,z}
Visceral organ	21,88 ±2,23^{b,y}	742,33 ±75,54^{d,z}	1,23 ±0,06^{a,z}	<0,818^{a,z}	184,03 ±17,63^{c,x}
Gill	34,31 ±4,88^{b,z}	916,67 ±77,19^{d,z}	1,04 ±0,07^{a,z}	<0,818^{a,z}	191,26 ±9,73^{c,x}

*There is a statistical difference between the values expressed with different letters in the same column (a, b, c) and the same row (v, y, z) (p<0.05).

The highest concentration in the liver tissue was Fe (916,67±77,19 µg.kg^{-1}), and the sorting for the highest concentration to the lowest was Fe>Zn>Mn>Cu>Co (p<0.05). The highest concentration in the muscle tissue was Fe (82,84±7,11 µg.kg^{-1}) and the sorting for the highest concentration to the lowest was Fe>Zn>Cu>Co>Mn (p<0.05). The highest concentration in the gonad tissue was Zn (418,75±54,11 µg.kg^{-1}) and the sorting for the highest concentration to the lowest was Zn>Fe>Mn>Cu>Co (p<0.05). The highest concentration in the visceral organs was Fe (742,33±75,54 µg.kg^{-1}) and the sorting for the highest concentration to the lowest was Fe>Zn>Mn>Co>Cu (p<0.05). The highest concentration in the gills was Fe (916,67±77,19 µg.kg^{-1}) and the sorting for the highest concentration to the lowest was Fe>Zn>Mn>Co>Cu (p<0.05). Zn concentration was determined at high levels in all tissues and organs studied, the lowest Zn concentration was determined in the muscle tissue.

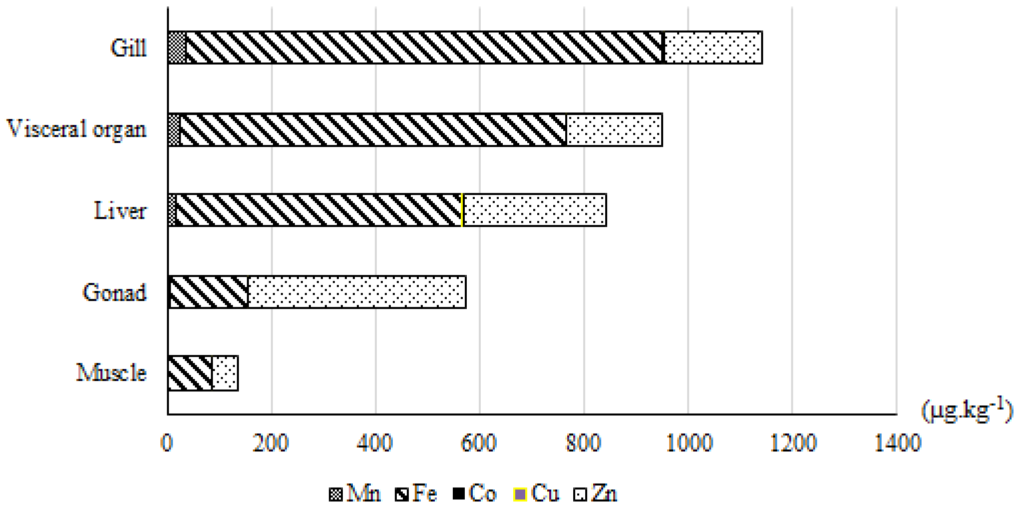

Figure 5. The frequency distribution of the whiting fish samples (µg.kg^{-1})

As seen in Figure 5, the tissue with the highest total metal accumulation was the gill, and the sorting for the highest metal concentration to the lowest was gill>visceral>liver>gonad>muscle. The measured heavy metals and their concentrations were compared to the FAO and FAO/WHO standards and are presented in Table 2.

The reported maximum copper level permitted by FAO for fish is 30 µg.g^{-1} (FAO, 2010). The copper levels in the samples in the present study were found to be lower than the permitted legal limits. The maximum acceptable Zn level reported by FAO for fish is 30 µg.g^{-1} (FAO, 2010). The Zinc levels in the samples in the current study were determined to be lower than the legal limits.

Comparing the heavy metal species and concentrations measured in the study to the specified national and international standards, the heavy metal concentrations determined in all tissues and organs of the researched fish samples were determined to be below the critical level specified in the standard, and no problems were determined in terms of public health. The Cu and Zn concentrations determined for muscle tissues of the fish were determined to be below the limit values recommended by FAO, FAO/WHO (Table 3).

Table 3. Comparison of the average metal concentration results of the current study (µg.kg^{-1} dry weight) and legal standard limits in whiting fish (*Merlangius merlangus*, Linnaeus, 1758) from the Turkish Coast of the Black Sea

		Mn	Fe	Co	Cu	Zn	References
Whiting fish		<0,413	82,836	<0,479	<0,818	50,452	This study$^{\Delta}$
	Standard	-	-	-	30,00*$^{\Delta}$	30,00*$^{\Delta}$	FAO, 2010**
		-	-	-	30,00*$^{\Delta}$	40,00*$^{\Delta}$	FAO/WHO, 2004**

*wet weight µg.g^{-1}; $^{\Delta}$muscle tissue **from Mutlu, 2021

A correlation matrix was calculated for the concentrations of different heavy metals in whiting fish tissues from the Black Sea and is given in Table 4.

Table 4. Correlation analysis results of heavy metal analyzes

	Mn	Fe	Co	Cu	Zn
Mn		**	*		
Fe	0,77**				
Co	0,743*	0,508			
Cu	-0,533	-0,181	-0,159		
Zn	-0,263	0,35	-0,240	0,367	

*Correlation is significant at the 0.05 level

** Correlation is significant at the 0.01 level

Positive high correlations ($p<0.01$) were determined between Mn and Fe, high positive correlations were determined between Mn and Co ($p<0.05$), and low negative correlations were determined between Mn and Cu and Zn ($p>0.05$). Positive low correlations were found between Fe and Co and Zn, negative low correlations were determined between Fe and Cu, negative low correlations were determined between Co and Cu and Zn, and low positive correlations were found between Cu and Zn ($p>0.05$).

According to the results of the study, for the Black Sea not to experience further land-based pollution problems in the future, it is recommended to implement the already-overdue environmental measures immediately and to control the implemented these measures and make them sustainable. The results revealed that, rather than the muscle tissue, the heavy metal accumulations were higher in other measured tissues and organs (liver, gill, visceral organ, and gonad). Gökkurt Baki reported a similar finding for the same species in their study carried out in 2021 (Gökkurt Baki, 2021). The researcher conducted the study aiming to determine the accumulation of the Cd, Cr Ni, Pb, and Hg metals in various tissues and organs of whiting fish, and have reported that the heavy metal accumulations in gills, visceral organs, and livers, except for the gonad, were at higher concentrations compared to those in the muscle tissues. Also, the highest concentration was determined in the gills in the cited study, and, similarly, the highest accumulation concentration was determined in the gills in the present study (Figure 5).

4. Conclusion

The metal accumulations in the tissues and organs of fish and/or metal concentrations to which they are exposed will also vary according to their living environments. Heavy metal exposure of fish should be evaluated concerning the release of heavy metals into the water as a result of anthropogenic processes, and the feeding habits and habitats of the fish. Therefore, in the present study, the whiting fish species living in a benthic environment were chosen and research was carried out accordingly. The results obtained in the study showed that, for the Black Sea where the level of land-based pollutants is high, the Cu and Zn levels were below the limits that can be considered dangerous according to the standards (FAO/WHO, 2004; FAO, 2010).

In line with the results obtained in the study, the heavy metal concentrations determined especially in the muscle tissues of whiting fish samples were generally below the standards, and therefore, it was concluded that they are at levels that will not affect human health yet. Accumulations in tissues other than muscle show variations. Especially the heavy metal measurements obtained in the gonad tissue must be a potential subject of future planning.

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